TITLE: Development of a Low Cost Moderately High Strength Tough Fiber for Industrial Applications

Project Number: G95-08

Investigators:
Steven B. Warner (UMass-Dartmouth)
Malcolm Polk (GA Tech)
Behnam Pourdeyhimi (GA Tech)
Haskell W. Beckham (GA Tech)
David Grubb (Cornell U)

Graduate Students:
Shawn Jenkins
Shalini Thadani
Matthieu Paindovaine

Project Goal: To develop a low cost fiber with the mechanical properties of spider silk: a tenacity of about 15 g/d and an elongation to break of about 20%

ABSTRACT

This project was initiated in March 1995 to develop a fiber that fills the gap between low priced industrial nylon or polyester (tenacity about 9 g/d) and high cost high tenacity reinforcement fibers (tenacity about 25 g/d) such as liquid crystalline or gel spun fibers. These properties are remarkably similar to those of spider dragline silk and one approach to the project is to understand and mimic with a synthetic polymer the morphology of silk. Another approach is based on the observation that silk goes through a lyotropic state in the spider spinneret. Hence, other liquid crystalline polymers with the appropriate chemical structure may be capable of both high strain-to-fail as well as moderately high tenacity. Other approaches based on solid state polymerization and, in particular. crosslinking within crystalline domains are also being considered. The work conducted to date has been largely identifying and gathering appropriate literature, speaking with recognized experts. and planning work. Creep studies, torsion pendulum and thermal analysis, creep testing, transmission electron microscopy, atomic force microscopy, and Raman spectroscopy on spider fibers are planned or have commenced. Work is well along on synthesizing appropriate liquid crystalline polymers in sufficient quantities to spin fibers.

INTRODUCTION

The achievement of both moderate tenacity and moderate strain-to-fail leading to a tough fiber has eluded man: however, the lowly spider routinely spins lyotropic aqueous solutions [1] of proteinaceous material into fibers with such properties. While a great deal of effort is currently directed towards determining the amino acid sequencing in spider silk (Kaplan, Fossey, et al at Natick Labs and a plethora of others [2]), little attention has been directed towards elucidating the role of morphology in providing the excellent mechanical properties. Only Termonia [3] at DuPont and Jaffe [4] at Hoechst-Celanese seem to have projects directed towards mimicking morphology rather then polymer chemistry. In a late 1994 paper Termonia suggests that the small P-crystallite size plays a key role in the mechanical properties of spider silk; however, the suggestion has yet to be substantiated. (Spider silk can be envisioned as a reinforced rubber; however, it is difficult to understand the origin of the high tenacity.) On the other hand, Irwin [5] at DuPont published in a recent paper that certain liquid crystalline polymers may be capable of allowing unraveling of chains from crystalline regions during deformation. Such an unraveling may allow for the unique combination of moderate tenacity and toughness.

Other approaches to increasing the strength of conventional polymers may be lead to fibers with the target properties. Crosslinking within crystalline domains has shown promise on otherwise not so strong samples [6]. Solid state polymerization of condensation polymers also has potential to increase strength [7]. While the technique has been used successfully in thermotropic polyesters, no increases in strength have yet been realized in flexible chain polymers [7,8]

CONTACTS

Faculty on the project have visited Natick Labs to meet with S. Fossey and D. Kaplan (editor of Silk **Polymers,** reference 2). They have encouraged cooperation on all fronts and we have had extensive e-mail communications. (Note that their effort is largely designed to determine the sequence of amino acids groups along the polypeptide chains with the aim of producing spider silk chemistry by other means. Hence, there is little or no competition.) Dr. Kaplan suggested that a student might spend some time at Natick Labs silking spiders for our needs as well as for some of his needs. The student would also be able to use some of Natick's instrumentation.

Contact was also made with M. Jaffe at Hoechst-Celanese [4]. His efforts are directed largely parallel with ours. His group has been actively working on this project for about a year. In March, just before this project was funded, Dr. Jaffe hosted many of the eminent spider scientists at Hoechst-Celanese for an information exchange. We hope to participate in the next meeting, if not host it ourselves.

Many relevant up-to-date papers have been gathered and scrutinized. Ongoing literature searches, meetings with other experts. and participation on conferences will keep the group abreast of new developments.

THERMOTROPIC POLYMERS

Liquid crystal copolyesters based on 2-chiorohydroquinone is a system that we have chosen to initially investigate. Specifically, we synthesizing poly[oxy(2-chloro-1,4-phenylene)oxyterephthaloyl-co-oxymethylene-1,4-cyclohexylenemethylene-oxyterephthaloyl]. It is prepared by the reaction of 2-chlorohydroquinone and 1,4-cyclohexanedimethanol with terephthaloyl chloride in a mixture of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. So far, we have prepared 160g of polymer. When we have ca. one pound of polymer we will melt-spin fibers and determine mechanical properties. The Bradford University Small Scale Fiber Extrusion equipment has been ordered.

TRANSMISSION ELECTRON AND ATOMIC FORCE MICROSCOPY

While some results have been published on TEM of spider silk [9], corroboration of these as well as other results is necessary, in part because the information is new and especially because a range of values for measured parameters are cited. Calculations based on the know sequencing of spider silk have been conducted a priori to estimate the upper bounds of crystallite size and percent crystallinity. TEM samples are being prepared using simple techniques such as cryogenic grinding.

We are also currently negotiating with Digital and Burleigh Instruments on their AFM equipment. Before the end of the summer, we will have an AFM to study the surface morphology of silk and other fibers. Although AFM probes the surface of fibers on a fine scale, the surface morphology is usually a reflection of the underlying morphology. A recent paper based on AFM results by a group at DuPont [10] suggests a entirely different structure for silk than was generally accepted. It is important to compare their findings with other resul.s [11].

RAMAN SPECTROSCOPY

Raman spectroscopy is being utilized to determine whether crystallite size, orientation, and crystallinity change with elongation or retraction. (Spider dragline silk fibers contract when exposed to aqueous solutions, since the water partially solves the polymer and allows entropic shrinkage of the oriented chains.) It is very important to ascertain whether crystallinity increases with elongation. If chains unravel, crystallinity will decrease. If there is strain-induced crystallization, crystallinity will increase. It is critical that we begin to understand the rather unusual stress-strain behavior at high elongation [12]. Preliminary Raman results show negligible change in crystallinity with elongation.

TORSION PENDIJLUM AND THERMAL ANALYSIS

A torsion pendulum capable of heating and environmental control is being set up to probe the structure and properties of spider silk. One key property of spider silk is its glass transition temperature. Current literature suggests that it may as much as 100°C below room temperature or more than 200°C above room temperature [13,141. The torsion pendulum will provide data on tan δ, or the loss in the polymer, and also on G, the shear modulus. The ratio of E/G provides vaiuable insight into the structure of fibers. High modulus fibers such as poly(para-phenylene terephthalamide), PPTA. show a very high E/G due to a ftbrillar structure. The high E/G is largely responsible for the low compressive strength of such fibers [15]. Spider silk, on the other hand, is characterized by a high compressive strength [11] and a debatably non-Iibrillar morphology [2,10,11,14].

CREEP RUPTURE

Creep beh.avior is also provides indirect information on the morphology of fibers. For example, crosslinkcd fibers show little creep. Spider silk contains a small amount of cysteine bonds, which provide some crosslinking. PPTA fibers also shows good creep resistance, presumably in part because of the extensive hydrogen bonding. Like PPTA, spider dragline silk has extenisve hydrogen bonding.

A creep-rupture device has been built to perform experiments on newly formed (silk) fibers. It will be tested within the next couple weeks. The setup consists of three platforms. The upper one includes two rows of switches (12 on each row). The middle platform is moved up and down using a stepper motor that is attached to the lower platform. Initially, the fibers are held by the switches at one end and attached to individually tailored weights at the other. The weights are initially placed on the middle platform positioned such that the fibers are not fully extended (the fibers are not stressed). When the motor lowers the middle platform, the fibers will become fully extended and the corresponding switches will close. The time the state of the switch is changed is stored as the starting point for that fiber. When that fiber breaks, the corresponding switch ill open triggering a change of state of the switch. The difference between the two changes will be the time-to-failure for that particular fiber. The time-to-failure data for all fibers are stored on disk while the experiment is in progress. the time-to-failure data is accurate to within a few milliseconds.

The interface for this setup is accomplished using National Instruments+ PC DIO 96 Data Acquisition Board (DAQ). The 24 switches are monitored by 24 digital input lines which indicate whether a particular switch is open or closed. The stepper motor that controls the middle platform+s motion is interfaced with the computer using the P51 series driver from American Precision Industries, Inc. Through 8 digital lines connected to the driver, the computer software can control things such as direction (CW/CCW), stepping mode (full/Half), reset, no power (emergency stop), and can output step counts.

The software for this project consists of a Graphical User Interface (GUI) which displays the state of the switches and provides options for the control of the experiment. The software is written using National Instruments+ LabWindows/CVI development tool. This is a +C+ programming environment integrated with an appropriate user interface editor for building instrumentation systems.

SOLID STATE POLYMERIZATION

Incorporation of diacetylene groups into the backbone of linear polyamides provides a route for post-processing modification of the material properties of these polymers [6].Through standard room temperature solution processing methods, fibers and films may be produced. Exposure of the products to fixed dosages of electron-beam radiation activates the diacetylene groups for controlled crosslinking of the host polymer chains. The crosslinking takes place via solid state cross-polymerization of diacetylenes to polydiacetylenes across the host polyamide chains. Due to the topological nature of this reaction, the cross links are primarily restricted to the ordered crystalline regions, although this depends on the radiation dosages employed, the structure being irradiated, and the irradiation conditions [16]. Crosslinking proceeds without the formation of volatile byproducts. A diacetylene-functionalized polyamide fiber, poly(hexamethylene 10,12-docosadiyn-1,22-diamine), has been evaluated for both drawn and undrawn samples as a function of radiation dosage [17]. Resonance Raman scattering has shown that the polydiacetylenes do in fact exist in the cross-polymerized polyamide fibers. Interference microscopy has shown that the refractive index normal to the fiber axis increases with radiation dosage, exactly what is expected if the highly polarizable polydiacetylene chains were created along this axis. Dynamic mechanical analyses prove that crosslinking, which is accompanied by up to 100% enhancements in ultimate tensile strength [18] does not restrict the mobility of the amorphous regions as evidenced by unchanged tan δ curves upon irradiation of the fibers. This would be expected if the cross links were produced in the crystalline regions.

Solid state polymerization of the bulk polymer has been used for decades to increase the molecular weight of polyester and nylon chip [19]; however, increases in fiber tenacity during solid state polymerization have only been realized on thermotropic polymers with appropriate end groups [7,8]. When oriented flexible chain condensation fibers are solid state polymerized, entropic shrinkage forces lead to shrinkage. Restrained fibers still have sufficient mobility to allow chain folding. Abhiraman et al [19] attempted to circumvent the shrinkage problem by solid state polymerizing partially oriented (high speed spun) fiber and post drawing. The results did not give the high strength hoped for (re. more than 10 g/d).

We have contemplated solid state polymerization of as low a molecular weight nylon or polyester fiber as can be made; however, solid state polymerization is a thermally activated process. Such fibers. which presumably will have no chain folds, will not survive normal solid state polymerization conditions. Hence, we continue to contemplate a workable plan along these lines.

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